



## Recent progress in perfluoroalkyl-phosphorus chemistry



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### ABSTRACT

Electrochemical fluorination (Simons process) provides a cheap industrial access to a series of tris(perfluoroalkyl)difluorophosphoranes. These substances are a convenient starting material for the preparation of various perfluoroalkyl-phosphorus compounds. The preparation of a variety of new salts and ionic liquids with perfluoroalkyl-fluorophosphate (FAP) and perfluoroalkyl-phosphinate anions is described. The tris(perfluoroalkyl)difluorophosphoranes,  $(R_F)_3PF_2$ , are strong Lewis acids which are of interest for the application in catalysis. The syntheses of various derivatives of bis(perfluoroalkyl)phosphinic acids,  $(R_F)_2P(O)OH$ , are presented.

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## 1. Results and discussion

Phosphorus trifluoride,  $PF_3$ , and phosphorus pentafluoride,  $PF_5$ , were the first perfluorinated phosphorus compounds described in the literature [1,2]. Today  $PF_5$  is produced in multi-ton quantities and mostly used for the synthesis of lithium hexafluorophosphate,  $LiPF_6$  – the most commonly used conducting salt in lithium-ion batteries [3]. A major drawback of  $LiPF_6$  based electrolytes is their poor stability at elevated temperatures due to the elimination of  $LiF$  and the generation of  $PF_5$ :  $LiPF_6 \rightleftharpoons PF_5 + LiF$  [3].  $LiPF_6$  is moisture sensitive (Scheme 1) [3].

The limited thermal and hydrolytical stability of  $LiPF_6$  require a development of safer conducting salts for the application in Li-batteries.

Perfluoroalkyl phosphorus compounds have been synthesized more than 60 years ago.

Haszeldine et al. [4] have reported the preparation of tris(trifluoromethyl)phosphine,  $(CF_3)_3P$ , by the reaction of  $CF_3I$  with white phosphorus in an autoclave at 200–220 °C. Surprisingly, the reaction of  $C_2F_5I$  and  $C_3F_7I$  with white phosphorus does not result in the formation of tri-substituted phosphines,  $(R_F)_3P$  [5,6]. Alternatively to the autoclave reaction, tris

(trifluoromethyl)phosphine,  $(CF_3)_3P$ , can be prepared by the reaction of triphenylphosphite,  $(PhO)_3P$ , with  $CF_3Br/(Et_2N)_3P$  (Ruppert reagent:  $[(Et_2N)_3P-Br]^+ [CF_3]^-$ ) in hexamethylphosphoramide, HMPA (Scheme 2) [7].

The polar solvent hexamethylphosphoramide (HMPA) is required in this synthesis. The reported yield of  $(CF_3)_3P$  is good (up to 85%), but the use of this toxic solvent and commercially not available trifluoromethyl bromide are serious drawbacks for this protocol. Tris(trifluoromethyl)phosphine can be oxidized to  $(CF_3)_3PCl_2$  by  $Cl_2$  and converted to  $(CF_3)_3PF_2$  by fluorination with  $ZnF_2$  [7].

Trifluoromethyl derivatives of phosphorus are not very stable compounds. Mahler has reported the gradual decomposition of  $(CF_3)_3PF_2$  to  $PF_5$  via elimination of difluorocarbene,  $:CF_2$  (Scheme 3) [8].

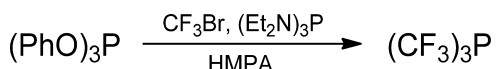
This process is slow at room temperature, but significantly accelerated at elevated temperatures. Difluorotris(trifluoromethyl)phosphorane,  $(CF_3)_3PF_2$  decomposes at 25 °C in the gas phase at a rate of 0.5% per month. At elevated temperatures (100 °C) the decomposition is much faster (40% within 17 h) [8]. The handling of the reduction product  $P(CF_3)_3$  requires special safety precautions because  $P(CF_3)_3$  (b.p. 17 °C) reacts violently on contact with air (see Fig. 1a) [9,10].

In contrast to  $(CF_3)_3P$ , the higher homologue  $(C_2F_5)_3P$  is much more stable (Fig. 1b). It can be handled by standard Schlenk techniques under nitrogen or argon. Tris(pentafluoroethyl) phosphine can be readily prepared by the reduction of tris

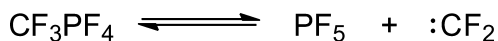
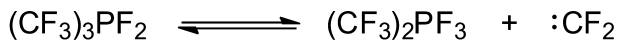
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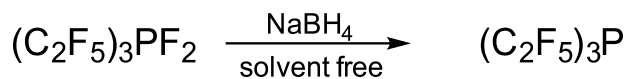
Scheme 1.



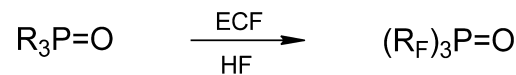
Scheme 2.



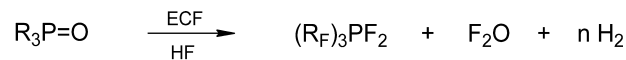
Scheme 3.



Scheme 4.

R = C<sub>2-8</sub> alkylR<sub>F</sub> = C<sub>2-8</sub> perfluoroalkyl

Scheme 5.

R = C<sub>2-6</sub> alkylYield: 24-46% R<sub>F</sub> = C<sub>2-6</sub> perfluoroalkyl

Scheme 6.

(pentafluoroethyl)difluorophosphorane with NaBH<sub>4</sub> or other reagents (Scheme 4) [11].

Tris(pentafluoroethyl)difluorophosphorane, (C<sub>2</sub>F<sub>5</sub>)<sub>3</sub>PF<sub>2</sub>, is nowadays produced in multi-ton quantities by the electrochemical fluorination (Simons process, ECF) of triethylphosphine [12,13]. Tris(pentafluoroethyl)difluorophosphorane is a clear and colorless liquid. It can be distilled (b.p. 91–92 °C) at atmospheric pressure without decomposition. NMR spectroscopic data of (C<sub>2</sub>F<sub>5</sub>)<sub>3</sub>PF<sub>2</sub> confirm a trigonal-bipyramidal structure with two equivalent fluorine atoms on the axial positions and the three C<sub>2</sub>F<sub>5</sub> groups in the equatorial position (see Fig. 2).

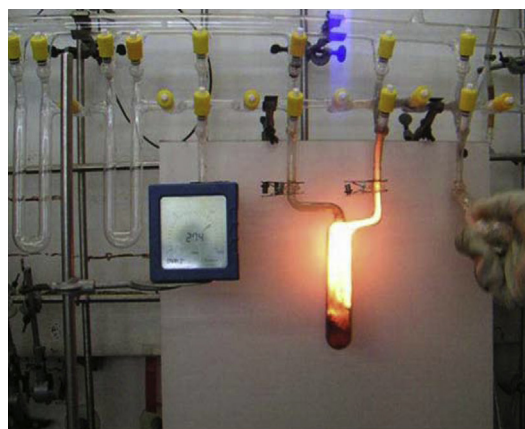
The first example of the electrochemical fluorination of an organophosphorus compound was reported by Yagupolskii et al. [14] (Scheme 5).

Tris(perfluoroalkyl)phosphine oxides were identified as products formed in the electrochemical fluorination of trialkylphosphine oxides. Later it was found out that the main products in this process were not tris(perfluoroalkyl)phosphine oxides but tris(perfluoroalkyl)difluorophosphoranes (Scheme 6) [15].

The disadvantage of the electrochemical fluorination of trialkylphosphine oxides, however, is not only the low yield of the product, tris(perfluoroalkyl)difluorophosphorane, but especially the formation of an equimolar quantity of the toxic gas, F<sub>2</sub>O, that in combination with H<sub>2</sub> (constantly produced during the ECF process) can cause a severe explosion. Using trialkylphosphines excludes the formation of F<sub>2</sub>O. The yield of the formed, tris(perfluoroalkyl)difluorophosphoranes is much better in comparison to the ECF of

trialkylphosphine oxides (Table 1) [12,13]. This technology provides a convenient protocol for the industrial production of (R<sub>F</sub>)<sub>3</sub>PF<sub>2</sub>. Tris(perfluoroalkyl)difluorophosphoranes are very reactive compounds. For example, (C<sub>2</sub>F<sub>5</sub>)<sub>3</sub>PF<sub>2</sub> readily reacts with lithium fluoride forming the corresponding lithium tris(pentafluoroethyl)trifluorophosphate, Li[(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub>PF<sub>3</sub>] (LiFAP) as an analog to lithium hexafluorophosphate, Li[PF<sub>6</sub>] (Scheme 7) [16,17].

LiFAP can be prepared *in situ* in polar solvents such as dimethyl carbonate (DMC) or ethylene carbonate (EC). These solvents are typical media for the preparation of electrolytes for Li-ion batteries. LiFAP is much more stable against hydrolysis in comparison to lithium hexafluorophosphate, Li[PF<sub>6</sub>]. After the addition of 500 ppm of water to a 1 M solution of LiPF<sub>6</sub> in EC:DMC (50:50 wt%) 250 ppm H<sub>2</sub>O were consumed within ca. 20 h and a corresponding amount (ca. 500 ppm) of HF was generated. In a similar experiment, after the addition of 1000 ppm of water to a 1 M solution of Li[(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub>PF<sub>3</sub>] (LiFAP) in an organic carbonate mixture the system remained unchanged for three days; no water consumption and no HF formation were detected [17]. A solution of LiFAP in EC:DMC (50:50 wt%) is slightly less conductive than a corresponding solution of Li[PF<sub>6</sub>], but the maximum conductivity (8.6 mS cm<sup>-1</sup>) for the LiFAP electrolyte is reached with a 0.8 M solution. For Li[PF<sub>6</sub>] in EC:DMC (50:50 wt%) the maximum conductivity (10.7 mS cm<sup>-1</sup>) was reported using a 1 M solution [17]. Lithium bis(pentafluoroethyl)tetrafluorophosphate, Li[(C<sub>2</sub>F<sub>5</sub>)<sub>2</sub>PF<sub>4</sub>] has a symmetrical structure and exhibits a slightly better conductivity in organic solvents when compared

a) (CF<sub>3</sub>)<sub>3</sub>P (b.p. 17 °C)b) (C<sub>2</sub>F<sub>5</sub>)<sub>3</sub>P (b.p. 85-87 °C [11])Fig. 1. (C<sub>2</sub>F<sub>5</sub>)<sub>3</sub>P is more safe to handle in comparison to (CF<sub>3</sub>)<sub>3</sub>P.

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